

Convenient, Low Energy, Solid-Liquid Metathesis Reactions; Synthesis of TiN, TiO₂, VN, VO₂ and Ti_xV_yN ($x + y = 1$)

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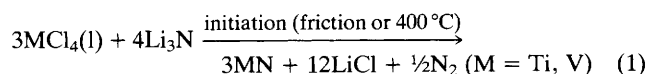
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Thermal or frictional initiation of mixtures of MCl₄(l) (M = Ti, V) and Li₃N or Li₂O produce MN, Ti_xV_yN or MO₂ *via* a rapid, exothermic, solid-liquid metathesis reaction.

Metal nitrides and oxides are ceramic materials used industrially for a variety of processes including catalysis, reflectance devices, hardness coatings, engineering materials and refractory linings.¹⁻³ They are conventionally made by combining the elements at high temperature (600–1400 °C), by hydrothermal/ammonolysis processes, electrochemical synthesis or by molecular precursor routes.⁴⁻⁷ Self-propagated high temperature synthesis routes to metal sulfides and phosphides have been developed by Russian chemists wherein compacted elemental powders are ignited to promote an exothermic reaction.⁸ Recently this work has been taken up in the West and Kaner and coworkers have demonstrated the ease of solid-state metathesis reactions to form metal sulfides, phosphides and arsenides from reactions of group 1 or 2 pnictides/chalcogenides with metal halides.⁹⁻¹² We illustrate here that the metathesis reactions are not restricted to pressed solid powders or preground powders but can be achieved by using metal halide liquids with Li₃N and Li₂O, rare examples of solid-liquid heterogeneous metathesis reactions. Further

the ease with which the initial liquid reagents can be mixed allows for extremely facile synthesis of mixed metal nitride lattices at low initiation temperature.

Conventional oven (400 °C) initiation of the reaction between TiCl₄(l) or VCl₄(l) and Li₃N(s) in a sealed evacuated quartz ampoule produces TiN or VN respectively in reasonable yield (50–60%), *via* a rapid (2–3 s) exothermic solid-liquid metathesis reaction [eqn. (1)]. The black product from



the reaction is spread over the ampoules walls. The reaction of VCl₄(l) or TiCl₄(l) and Li₃N can be initiated at room temp. on rapid stirring (frictional initiation) provided the reactions are above a certain scale (0.3 g of Li₃N); great care should be taken in such reactions which are potentially explosive.

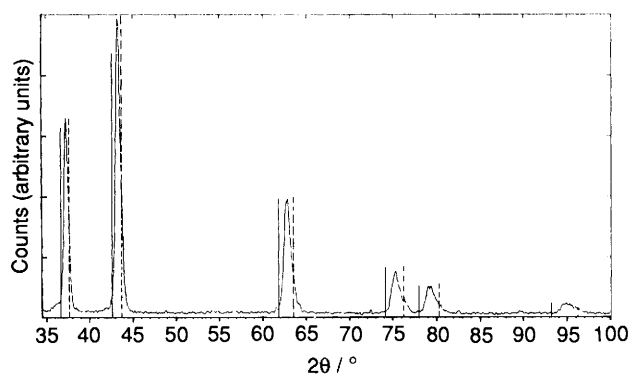


Fig. 1 X-Ray powder diffraction trace from reaction of equimolar amounts of TiCl_4 and VCl_4 with Li_3N after thf trituration, (—) standard pattern for TiN, (---) standard pattern for VN

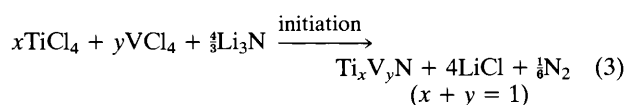
Scanning electron microscopy (SEM) analysis† of the powder from either frictional or thermal initiation reveals a smooth surface consistent with a $\text{LiCl}(\text{s})$ coating, this is also confirmed by energy dispersive analysis by X-rays (EDAX) which shows the presence of metal, nitrogen and some chlorine. Triturating the black powder with tetrahydrofuran (thf) or water removes the LiCl (no chlorine present by EDAX analysis) and leaves micron sized particles with sharp angles and faces. Nitrogen, as predicted by eqn. (1) was observed by GC.

Reactions of $\text{TiCl}_3(\text{s})$ with Li_3N proceed analogously to the $\text{TiCl}_4(\text{l})$ reactions [eqn. (2)] except the solid-state metathesis



reaction produces fused black lumps of product coating the ampoules walls. The products from either reaction [eqns. (1) and (2)] after thf trituration are phase pure TiN as determined by X-ray powder diffraction‡ (XRPD) and standardised EDAX analysis. The Scherrer equation¹³ gives average crystallite particle sizes of 300–350 Å for these powders. FT-IR analysis§ of the powders reveals a weak band centred at 450 cm^{-1} corresponding to a M–N stretch whilst the magnetic moment measurements¶ of the metal nitrides agree well with literature values.¹⁴

Thermal initiation of a mixture of $x\text{TiCl}_4(\text{l})$, $y\text{VCl}_4(\text{l})$ and Li_3N produces the mixed metal nitrides $\text{Ti}_x\text{V}_y\text{N}$, in a stoichiometrically controlled fashion [eqn. (3)]. The X-ray



diffraction (XRPD) pattern of $\text{Ti}_x\text{V}_y\text{N}$ ($x = y = 0.5$) (Fig. 1) after thf trituration was phase pure and intermediate between the VN ($a = 4.139 \text{ Å}$) and TiN ($a = 4.232 \text{ Å}$) patterns with $a = 4.178 \text{ Å}$; whilst the EDAX step analysis showed constant ratios for Ti/V across the surface. The trituated metal nitride had satisfactory microanalysis with levels of lithium incorporation less than 0.05%.

The fact the $\text{TiCl}_4(\text{l})$ and $\text{VCl}_4(\text{l})$ are miscible liquids allows facile formation of ternary powders $\text{Ti}_x\text{V}_y\text{N}$. Conventionally

† SEM/EDAX analyses were obtained on a Jeol JSM 820 equipped with the KeveX System.

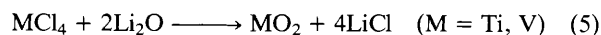
‡ XRPD were obtained on a Siemens D5000 diffractometer using Nickel filtered copper $\text{K}\alpha$ (1.5406 Å) radiation.

§ FT-IR were obtained on a Nicolet 205 (CsI) using pressed KBr or CsI discs.

¶ Magnetic moment measurements were determined by Johnson Matthey balance.

mixed nitride powders are made by alloying the metals and reacting with dinitrogen at elevated temperature or by reactions involving extremely long annealing periods. Attempts at forming mixed metal nitrides $\text{M}_p\text{M}'_q\text{N}_r$ by solid-state metathesis reactions involving Li_3N and solid metal halides requires long annealing times to form good solutions due to the poor intermixing of the starting materials.

Reaction of Li_2O with TiCl_3 , VCl_3 , TiCl_4 and VCl_4 were investigated analogously to the Li_3N reactions. The reaction is neither as spontaneous nor as rapid although heating sealed ampoules of the metal halides with lithium oxide did produce transition metal oxides (TiO_2 , VO_2 , V_2O_3) and a small amount of lithium metal oxides as assessed by XRD of the



trituated powder. The metal oxides were analysed by both XRPD and EDAX analysis which revealed only metal and oxygen after thf trituration. The TiCl_4 reaction produces white TiO_2 with a rutile lattice, in good yield, 60–70%.

The reactions of Li_3N and Li_2O with titanium or vanadium chlorides are exothermic typically with $\Delta fH^\circ = -900 \text{ kJ mol}^{-1}$ as assessed *via* Hess' law.¹⁵ A certain initiation temperature is required to stimulate reaction; this has been assessed as 310–325 °C by differential scanning calorimetry analysis in reactions involving Li_2O .

The ease of separation of either the metal nitride or metal oxide products in the reactions involving Li_3N or Li_2O , from co-produced LiCl , the rapid reaction (a few minutes), low energy initiation (400 °C/friction) and ease of forming mixed metal nitrides illustrate the utility of solid-state and solid-liquid metathesis reactions to form nitride and oxide based ceramics.

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References

- J. C. Bailer, H. J. Emeléus, R. Nyholm and A. F. Trotman Dickenson, in *Comprehensive Inorganic Chemistry*, Pergamon, Oxford, 1973, vol. 2, p. 233.
- L. Toth, *Transition Metal Carbides and Nitrides*, Academic Press, New York, 1971, p. 176.
- H. A. Johansen, in *Survey of Progress in Chemistry 8*, ed. A. Scott, Academic Press, New York, 1977, p. 57.
- R. M. Fix, R. G. Gordon and D. M. Hoffman, *J. Am. Chem. Soc.*, 1990, **112**, 7833.
- L. V. Interrante, W. Lee, M. McConnell, N. Lewis and E. Hall, *J. Electrochem. Soc.*, 1989, **136**, 472.
- C. Russel, *Chem. Mater.*, 1990, **2**, 241.
- C. Russel and M. M. Seibold, *J. Am. Ceram. Soc.*, 1989, **72**, 1503.
- V. I. Torbov, V. I. Chukalin and E. I. Yarembash, *Neorg. Mater. (Russ.)*, 1970, **6**, 1772.
- P. R. Bonneau, R. F. Jarvis and R. B. Kaner, *Nature*, 1991, **349**, 510.
- P. R. Bonneau, R. F. Jarvis and R. B. Kaner, *Inorg. Chem.*, 1992, **32**, 2127.
- R. E. Treece, G. S. Macala and R. B. Kaner, *Chem. Mater.*, 1992, **4**, 9.
- J. B. Wiley and R. B. Kaner, *Science*, 1992, **225**, 1093.
- H. P. Klug and L. E. Alexander, *X-Ray Diffraction Procedure for Polycrystalline and Amorphous Materials*, Wiley, New York, 2nd edn., 1974.
- B. R. Brown, in *Mellors Comprehensive Treatise on Inorganic and Theoretical Chemistry* Longmans, London, 1964, vol. VIII, supplement I, N (Part 1), p. 151.
- D. D. Wayman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Harlow, S. M. Bailey, K. C. Chumey and P. L. Nuttal, *The N.B.S. Tables of Chemical Thermodynamic Properties*, ACS, Washington DC, 1982.